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Fine Fibers by Extrusion and Subsequent Dissolution of Major Component

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This invention relates in general to synthetic fibers and in particular to a process for making synthetic fibers having extremely small cross-sectional areas and to the ultra-fine fibers so produced including improvements in the physical configuration of said fibers whereby their uses have increased scope. The term "ultra-fine fiber" as employed in the specification and in the claims is intended to designate and include fibers produced from truly synthetic thermoplastic resin materials, as distinguished from animal or natural cellulosic fibers or so-called "regenerated" cellulose fibers, and includes products which are molecularly oriented as well as those which are crystalline or amorphous. The average diameters of these ultra-fine fibers, assuming a cylindrical shape, are in the range of 0.1 micron to 5.0 microns.

Heretofore it has been proposed to produce ultra-fine plastic fibers by the action of a high velocity jet of gas on molten resin material. Generally the method consisted of heating an organic polymer to a highly fluid condition (usually in an inert atmosphere), spreading a thin film of the heated polymer on a suitable surface which was also heated, and subjecting the film to a velocity and temperature controlled blast of inert hot vapor or gas discharged as a jet across the exposed surface of the film. The jet of hot vapor or gas draws out from the surface small globules of resin which are attenuated by the force of the jet stream into ultra-fine fibers. As the fibers are being drawn by the gas stream, cooling occurs to a point where they become rigid and are broken into segments by the turbulent action of the stream of suspending gas. These segments are collected on a screen, or other suitable surface, where they form a highly entangled mat. The fibers are utilized in this form.

Owing, however, to the excessive heat required to attain sufficient fluidity of the plastic to allow drawing by air, serious decomposition may take place which results in a lowering of the molecular weight. Degradation of molecular weight results in an impairment of physical properties of the final fiber.

Furthermore, fibers of uniform diameter are difficult to obtain. Frequently the fibers produced have a large globule of resin at one end formed by a relaxation of the polymer and a consequent "balling-up". Some fibers may break off from the film surface before being sufficiently attenuated, or pellets of plastic may be pulled free from the film surface without being attenuated at all and be deposited in the fiber mat.

Still further, cold drawing of the fibers to induce molecular orientation is limited or non-existent due to the extremely tenuous inter-relation between fiber size, temperature of the molten plastic, and velocity of the suspending gas stream which must be

maintained.

It is therefore a general object of the present invention to provide a method for producing ultra-fine fibers more economically and in an orderly bulk form, heretofore not possible by prior processes, which permits new and novel uses for such fibers.

It is another object of the invention to provide a product more uniform in physical properties and general configuration and possessing superior mechanical properties.

A further object of the present invention is to provide synthetic ultra-fine fibers which may advantageously be utilized as a filtering medium in aerosol filtration, as a plastic fiber additive to paper and paper-like products, and as a liquid hold-up material similar in function to absorbent cotton.

It is a specific object of the invention to produce ultra-fine fibers of polyethylene, polychlorotrifluoroethylene, and polyamides of the nylon type.

According to the process of the present invention, ultra-fine fibers of improved characteristics, properties and uses are made by extruding a mixture of two or more normally solid, mutually incompatible thermoplastic resins to form a composite monofilament having as the minor component, the resin material from which the ultra-fine fibers are formed, and dissolving out the major resin component, with a solvent in which the minor component is insoluble, or at least only very slightly soluble.

The thermoplastic resins which may be employed in the present invention include all of the normally solid fiber-forming resins from which conventional size fibers used in the textile and paper industries may be produced by ordinary melt extrusion operations. Typical resins are polyethylene, the polymers of styrene, both atactic and isotactic, and the alkyl and halogen substituted styrenes, polymers of methacrylic esters such as polyethylmethacrylate, polymers of vinyl esters such as polyvinylacetate and polyvinylbutyrate, vinyl halide polymers such as polyvinylchloride, polyamides such as the nylons, fluoro vinyl polymers such as polytrifluorochloroethylene (a fluorothene), copolymers of styrene such as styrene and acrylonitrile copolymers, copolymers of vinyl halides and vinyl esters such as a copolymer of vinyl chloride and vinyl acetate, and copolymers of vinylidene halides and vinyl halides such as a copolymer of vinylidene chloride and vinyl chloride.

While it is possible to utilize a mixture of more than two resins in carrying out the present process to produce ultra-fine fibers of one component of the mixture, as a rule only two immiscible resins are required and two is the preferred number. Theory and practice show that if a mixture of one major and two minor components is extruded, and the major component is dissolved out, ultra-fine fibers of each of the two minor components are produced.

Generally speaking in combining the mutually incompatible resins prior to extruding them into the composite monofilament, conventional methods and apparatus are entirely suitable. If the resins are available as raw materials in powder or granular form having particle sized substantially uniform and equal as between the two or more resins, dry blending techniques such as those utilizing a conical blender or a ribbon blender are quite good. However, if the particle sizes of the individual resin materials are too dissimilar, poor mixing results from these methods. In this event hot processing methods may be employed.

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Fluxing the materials on a two roll mill or a Banbury mixer at a temperature dependent on the resins being handled produces suitable mixtures. Another means of mixing is to dissolve both or all of the starting materials in a suitable mutual solvent and then removing the solvent by evaporation. Still another method, practicable when resins are being used which show little tendency to degrade at temperatures near their melting point, is the so called "double extrusion" in which the materials are fluxed by a normal melt extrusion operation, pelletized or chopped after being extruded and dry mixed before the final extrusion into the composite monofilament form.

Particle size of the incompatible resins in a dry blended mixture affects the dimensions of the fibers ultimately obtained only when very little or no working of the mixture in the molten state is done prior to extrusion through an orifice to form a composite monofilament. If for example a mixture of two incompatible resins is charged into a heated cylinder equipped with a piston to force the molten mixture out through a small orifice with a minimum amount of milling of the mass, the dimensions of the fibers comprising the extruded filament can be controlled by correlating the particle size in the dry mixture with the dimension of the fibers produced, having set a fixed rate of filament attenuation. If there is no milling prior to or during extrusion, a proportional relation exists between fiber diameter and pre-extrusion particle size.

Normal operation, however, produces ultra-fine fibers. By normal operation is meant that at some point in the extrusion process the incompatible resins are fluxed in a plastic state to such an extent that initial particle size of starting materials is not a factor in determining the dimensions of the final fiber products. The amount of fluxing required is not large—the operation of the feeding screw in a conventional screw type extruder being sufficient. Hot processing the granulated resin mixture on a two roll mill or Banbury mixer before extrusion is sufficient even if a non-milling type ram or plunger extruder is used.

The relative volume of one resin component to the other in the composite monofilament is an important consideration in carrying out the present invention. In order to isolate the ultra-fine fibers of a given resin, that resin must be present in the composite monofilament in an amount less than 50 per cent by volume. Whereas fibers of the desired size may be formed from a given resin even though that resin is the major component of the monofilament, separation of these fibers from those of the minor resin component can not practically be accomplished by solvent extraction. As the composite monofilament is extruded and drawn, fibers of the major component resin are formed which in some instances completely surround one or more fibers of the minor component resin. If an attempt is made to selectively extract the minor component resin, these surrounding fibers effectively protect the encircled fibers from action by the solvent, producing undesirable non-uniform macro-fibers.

For a given composite monofilament composed of two mutually incompatible resins, the probability that the one resin chosen to be selectively extracted will be "sealed off" by the other resin component is lessened as the volume percentage of the resin to be extracted is increased. On the other hand if the resin to be extracted by solvent is present in too large a percentage by volume, the yield of the fiber product is too low from an economic standpoint.

In accordance with these principles, useful compositions for the composite monofilament may vary

from 10 to 45 parts by volume of one resin and from 90 to 55 parts by volume of the carrier resin. The preferred composition range, however, is 30 to 45 parts by volume of the resin from which the fibers to be isolated are composed and 70 to 55 parts by volume of the carrier resin.

Extrusion conditions, particularly temperature, will vary over a relatively wide range. The conditions depend on the physical and chemical properties of the extruded resin materials and thus may even vary for identical compositions according to the preference of skilled operators. However, the fluxed mixture of the incompatible resins must attain a melt fluidity in the extruder such that during the first drawing stage there is a smooth reduction of the diameter as the composite monofilament issues from the orifice and elongates while being hot drawn. While the extruded mix as it issues from the extruder nozzle does have a fibrous nature, attenuation is essential to produce ultra-fine fibers.

It is to be understood that whereas either hot drawing or cold drawing alone may produce fine fibers in a composite monofilament of two mutually incompatible resin materials, the results of each operation produce unique characteristics in the final fiber produced and may advantageously be employed in combination. Hot drawing, in the main, serves to reduce the diameter of the extruded monofilament thereby necessarily reducing the diameter of the individual fibers of which it is composed. After hot drawing, the fibers have little or no molecular orientation in a longitudinal direction.

The amount of hot processing or fluxing of the two mutually incompatible granulated resin starting materials will be a factor in determining the diameter of the fibers making up the composite monofilament at the moment it emerges from the extruder die. The difference in diameter between the bore of the extruder and the die orifice causes a certain amount of attenuation which may vary between extruder or for the same extruder depending on the size die that is attached. However, once the fluxing and extruding conditions for a given resin pair has been adopted, a single determination of the fiber size produced for a given amount of hot drawing is sufficient to establish approximately the amount of draw to produce fibers of a desired diameter. Assuming ideal characteristics for the individual fibers in the monofilament, i.e., that they are uniform rods, have circular cross-sectional areas, and elongate the same extent as the composite filament, the diameter of a fiber after drawing is equal to the diameter before drawing divided by the square root of the ratio of the new length to the old length.

Cold drawing may be included as an integral part of the over all process and follow immediately after the hot drawing or may be carried out at any time, even after storage of the composite monofilament, prior to dissolution of the carrier resin component. Cold drawing is primarily for the purpose of inducing in the ultra-fine fibers molecular orientation in a longitudinal direction. This "stretch orientation" as it is commonly called, is well known in the synthetic fiber art and the improvement in physical properties such as tensile strength and, in some instances, resistance to heat aging, which are thereby imparted to the fibers is also well known. However, the great difficulty involved in trying to stretch orient fibers having final diameters of not more than 5 microns either separately or in stranded bundles having no lateral attachments between fibers is completely overcome. The stretching of the composite monofilament is carried out in the same fashion as a unitary one-component filament of equal size. The degree of orientation imparted to the fibers is dependent on the polymeric material being used and uses to which the

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product will be put. Due to the relationship of the diameter to the length of a fiber before and after stretching, supra, cold drawing sufficient to induce several hundred per cent orientation does not greatly alter the fiber diameters even when hot drawing has previously reduced them to the desired range of 0.1 to 5 microns.

Since ultra-fine fibers of only one resin material are to be isolated from each pair of mutually incompatible resins extruded, the major component resin or the carrier resin may be chosen for a particular property displayed in relation to the solvent and the minor component resin. For instance polystyrene and polyvinyl acetate polymers process well with polyethylene and are also incompatible with polyethylene. They also have the added advantage of being readily soluble in cold solvents such as methyl-ethylketone or acetone. From an economic viewpoint the relative cheapness of these two solvents not only recommends them as preferred solvents but also adds to the suitability of polystyrene and polyvinyl acetate as carrier resins. They are similarly well suited for use as carriers of halogenated ethylene resins of the type represented by the so-called fluorothene or polychlorotrifluoroethylene resins.

It may not in all cases be possible to find a suitable incompatible resin carrier from the fluxing and extruding standpoint, which may also be readily extracted with a solvent. It is to be understood in these situations that the terms "dissolve" or "dissolution" or "extraction" are intended to have a sufficiently broad construction to include removal by virtue of chemical action in the same sense as zinc is said to dissolve in aqueous HCl. Even though the carrier resin may be destroyed by reaction with the solvent, factors such as the cost of the resin itself, or the possibility of operating without the need for special equipment to handle volatile organic solvents, may show this manner of extraction to be preferable to purely physical solution in the strictest sense of the word. For instance the low resistance of polyamides, such as the nylon type resins, to inorganic acids in addition to the good resistance of polyethylene to acid attack and further the mutual incompatibility of nylon and polyethylene are factors which when combined provide a convenient process for producing ultra-fine fiber of polyethylene by "dissolving-out" nylon from a nylon-polyethylene composite monofilament with concentrated HCl.

Further, a resin which serves as a carrier in one instance, may, by simply decreasing its content in the composite monofilament to a value below 45 per cent and at the same time increasing the content of other resins a comparable amount, become the resin which comprises the ultra-fine fibers. Thus it is as entirely practical to produce nylon ultra-fine fibers by dissolving out polyethylene with hot toluene as to make polyethylene ultra-fine fiber from a nylon-polyethylene composite of slightly different volume composition by reaction of an inorganic acid with the nylon.

In general normally solid, synthetic thermoplastic fiber forming resins are suitable for preparing ultra-fine fibers according to the present invention as long as at least two incompatible polymers, copolymers, or mixtures are extruded as a composite rod like shape and are capable of separation by selective extraction of the major component by solvent action. The resins may include, among others, and in addition to those previously mentioned, polyvinyl compositions and copolymers such as Saran (vinylidene chloride-vinyl chloride) and "Vinyon" HR (vinyl chloride-vinyl acetate); polyesters such as "Dacron" (polyethylene terephthalate); polyurethanes such as "Perlon U"; and polycarbonates.

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The composite monofilament from which the ultra-fine fibers are ultimately isolated may be either chopped into staple fiber lengths before treatment with solvent or it may be left in the same form as when extruded. It may be advantageous to weave or otherwise work the more manageable long, continuous monofilaments and then extract the carrier polymer leaving a processed article composed entirely of ultra-fine fibers. A tow of fibers is produced by treating with solvent a single continuous length of monofilament.

Diameters of ultra-fine fibers of many different polymers have been determined by observation with an electron microscope at magnifications up to 75,000X. Cross-sectional views show that the fibers are substantially circular, and longitudinal views show the fibers to be essentially uniform in diameter. The fiber diameters in the range of from 0.1 to 5 microns were determined not only by microscopic means, but were calculated from gas adsorption data for a cluster of fibers.

In the following examples operational details are given with respect to various fiber forming organic polymers for the purpose of further illustrating the invention, but not in limitation of the invention except as defined in the appended claims.

Example I

Ten parts by volume of polyethylene having an average molecular weight of approximately 21,000, in the form of $\frac{1}{8}$ inch pellets were tumbled together in a conical blender with 90 parts by volume of polystyrene, having an average molecular weight of approximately 55,000, also in the form of $\frac{1}{8}$ inch pellets. The pellet mixture was fed to a $\frac{1}{8}$ inch Hartig extruder operating under the following temperature conditions:

Front Barrel	- 450° to 500°F.
Back Barrel	- 150° to 160°F.
Nozzle	- 475° to 500°F.
Die	- 475° to 500°F.

The polymer mixture was extruded as a $\frac{1}{8}$ inch diameter composite monofilament at the rate of 4 to 5 pounds per hour and hot drawn over a godet at the rate of about 100 ft/min. At the end of the hot drawing, the composite monofilament had been uniformly reduced to approximately .050 inches in diameter. From the hot draw godet, the filament was sent through an ethylene glycol bath held at 250° to 270°F. to adjust the fiber temperature for proper cold drawing to induce longitudinal molecular orientation. Cold drawing was carried out at the rate of 500 ft/min. which resulted in approximately 400 per cent stretch orientation.

Pieces $\frac{1}{8}$ inch to $\frac{1}{2}$ inch chopped from the filament were immersed in methyl-ethylketone and sufficient time allowed for the polystyrene to dissolve. Substantially pure molecularly oriented polyethylene ultra-fine fibers were obtained having diameters in the range of from 0.5 to 1.0 micron.

Example II

A portion of the extruded filament from Example I prior to being cold drawn was immersed in methyl-ethylketone to dissolve out the polystyrene fibers. Substantially pure unoriented fibers of polyethylene having diameters in the range of from 0.5 to 1.0 micron were obtained.

Example III

Twenty parts by volume of polyethylene having an average molecular weight of approximately 21,000 in the form of $\frac{1}{8}$ inch pellets were tumbled together in a conical blender with 80 parts by volume of

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polystyrene having an average molecular weight of approximately 55,000 also in the form of pellets. The pellet mixture was extruded, hot drawn and cold drawn under identical conditions of Example 1. When immersed in methylethylketone, either before or after being stretch-oriented, the composite monofilament yielded ultra-fine fibers of polyethylene having average diameter of approximately 0.7.

Example IV

Forty parts by volume of polyethylene having an average molecular weight of approximately 21,000 and 60 parts by volume of polystyrene having an average molecular weight of 55,000 were processed and extruded according to the method of and under the same conditions as Example 1. One portion of the composite monofilament was hot drawn only and another portion was cold drawn in addition to being hot drawn. Samples of each portion were dissolved in methylethylketone. The polystyrene fibers were readily dissolved isolating non-oriented and oriented ultra-fine fibers, respectively. Substantially the same results were produced when the rate of hot drawing was increased from 100 ft./min. to 400 ft./min. and the cold drawing step excluded.

Example V

Sixty parts by volume of polyethylene having an average molecular weight of 21,000 and 40 parts by volume of polystyrene having an average molecular weight of 55,000 were processed and extruded according to the method of and under the same conditions as Example 1. Selective extraction of the polystyrene was not possible due to the masking effect of the polyethylene.

Example VI

Forty parts by volume of polyethylene having an average molecular weight of 21,000 and 60 parts by volume of polyvinylacetate (Bakelite's AYAA) were fluxed together on a two roll mill at 130°C. The mixture was cooled, chopped, and fed to a 1½ inch Hartig extruder. The extruder was operated under the following conditions:

Front Barrel	- 330°F.
Back Barrel	- <125°F.
Nozzle	- 330°F.
Die	- 330°F.

The polymer mixture was extruded as a .098 inch diameter composite monofilament and hot drawn at the rate of 30 ft./min. At the completion of the hot drawing step, the monofilament had been uniformly reduced to approximately .060 inches in diameter. From the hot draw godet, the filament was sent through a water bath held at 60 to 70°C to adjust the fiber temperature for proper cold drawing to induce longitudinal molecular orientation. Cold drawing was carried out at the rate of 105 ft./min. which resulted in approximately 250 per cent stretch orientation.

Pieces ¼ inch to ½ inch chopped from the filament were immersed in acetone and sufficient time allowed for the polyvinylacetate to dissolve. Molecularly oriented substantially pure polyethylene ultra-fine fibers were isolated having diameters in the range of from 0.5 to 1 micron.

Example VII

When the same materials as used in Example V are combined in the ratio of 60 parts by volume polyethylene to 40 parts by volume of polyvinylacetate and processed as in Example V, the complete extraction of the polyvinylacetate is not possible due to masking by the polyethylene. Few ultra-fine fibers can be isolated.

Example VIII

Twenty parts by volume of powdered fluorothene having a melt viscosity of about 10⁷ poises at 240°C. was combined with 80 parts by volume of polyethylene (average M.Wt. - 21,000) by sprinkling the fluorothene on the polyethylene sheeted on hot rolls at about 275°F. The sheeted material was chopped into ¼ inch to ½ inch pellets and fed to a 1½ inch Hartig extruder operating under the following conditions:

Front Barrel	- 560° to 600°F.
Back Barrel	- 150° to 250°F.
Nozzle	- 620° to 650°F.
Die	- 620° to 650°F.

The polymer mixture was extruded through a ¼ inch die at the rate of 4 to 5 pounds per hour and hot drawn at the rate of 75 ft./min. Chopped pieces of the extruded monofilament when treated with hot cyclohexane yielded substantially pure fluorothene ultra-fine fibers having diameters of approximately 3 microns.

Example IX

Twenty-five parts by volume of powdered fluorothene having a melt index of 10⁷ poises at 240°C. was mixed with 75 parts by volume of polyethylene (M.Wt. - 20,000 to 22,000) in the same manner as in Example VII, chopped into ¼ inch to ½ inch pellets, and dried at 200°F. for 2 hours. After drying the pellets were batch extruded by a procedure consisting essentially of feeding the polymer mixture into the chamber of a Van Dorn molding machine maintained at approximately 550° to 600°F., keeping the pellets for 2 to 4 minutes in the chamber and extruding the molten polymer mixture through a ¼ inch die at the rate of 20 ft./min. Without further drawing, the filament was treated with hot toluene to dissolve out the polyethylene. Ultra-fine fibers having average diameters of about 3 microns were isolated.

Example X

Twenty-five parts by volume of nylon (DuPont 45 FM-10001) and 75 parts by volume of polyethylene having an average molecular weight of 21,000 were mixed by tumbling and then dried at 180°F. in an air circulating oven for 2 to 3 hours. The dry mixture was fed to a 1½ inch Hartig extruder operating under the following conditions:

Front Barrel	- 530° to 550°F.
Back Barrel	- 150° to 200°F.
Nozzle	- 530° to 570°F.
Die	- 530° to 570°F.

The mixture was extruded through a .098 inch orifice at the rate of 4 to 5 pounds per hour and quenched in a cold water bath after traveling 2 inches in air at ambient temperature. After traveling 24 inches in the cold water bath, the filament was picked up on a godet having a peripheral speed of 75 ft./min. and then to a second godet operating at a speed sufficient to induce about 430 per cent stretch orientation. When treated with boiling toluene to dissolve the polyethylene, ultra-fine fibers of nylon were isolated having diameters in the range of 0.1 to 5.0 microns. Calculation of fiber diameter from data on surface area measurements determined by gas adsorption shows the average diameter value to be 0.8 microns. Electron micrographs of cross-sectional areas of filaments etched with hot toluene show the assumption of a cylindrical cross section for the fibers made for calculation purposes to be proper.

Example XI

75 Thirty-five parts by volume of nylon (DuPont

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FM-10001) and 65 parts by volume of polyethylene having an average molecular weight of 21,000 were treated according to the process of Example IX with the exception that the peripheral speed of the first godet was 50 ft/min. and the cold draw stretch orientation was 370 per cent. Extraction of the polyethylene with boiling toluene yielded ultra-fine fibers of nylon having diameters from 0.1 to 5.0 microns.

Example XII

Sixty-five parts by volume of nylon (DuPont FM-10001 and 35 parts by weight of polyethylene (M.Wt. - 20,000 to 22,000) were treated according to the process of Example IX with the exception that the peripheral speed of the first godet was 160 ft/min. and the cold draw orientation was 380 per cent. The nylon was extracted from the monofilament by treatment with concentrated hydrochloric acid. Polyethylene ultra-fine fibers were isolated.

Example XIII

The extruded composite monofilament from Example XI was woven into cloth on a Hand Skill loom. The cloth was treated with hot toluene until the polyethylene was dissolved out. A loosely woven cloth of ultra-fine nylon fibers resulted.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for making ultra-fine fibers of synthetic, thermoplastic, normally solid, resin material which comprises intimately mixing unequal parts by volume of two mutually incompatible, normally solid, thermoplastic resin materials, heat extruding said mixture to form a composite monofilament, and selectively dissolving out the major resin component thereby isolating ultra-fine fibers of the minor resin component.

2. A process for making ultra-fine fibers from a synthetic thermoplastic, normally solid resin material which comprises intimately mixing said resin material with a thermoplastic, normally solid carrier resin which is incompatible with said resin, said mixture comprising from between 55 and 90 parts by volume of the carrier resin and complementarily from between 45 and 10 parts by volume of the fiber forming resin, heat extruding said mixture to form a composite fibrous monofilament, drawing said composite fibrous monofilament to decrease the component fiber diameters to between 0.1 and 5.0 microns, and dissolving out the carrier resin to isolate the ultra-fine fibers.

3. A process as claimed in claim 2 in which the resin mixture comprises from between 55 and 70 parts by volume of the carrier resin and complementarily from between 45 and 30 parts by volume of the fiber forming resin.

4. A process as claimed in claim 2 in which the fiber forming resin is one of the group consisting of normally solid polyethylene, nylon, and polytrifluorochloroethylene.

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5. A process as claimed in claim 2 in which the fiber forming resin is normally solid polyethylene and the carrier resin is one of the group consisting of normally solid polystyrene and normally solid polyvinyl acetate.

6. A process as claimed in claim 2 in which the fiber forming resin is normally solid polytrifluorochloroethylene and the carrier resin is normally solid polyethylene.

7. A process as claimed in claim 2 in which the fiber forming resin is normally solid nylon and the carrier resin is normally solid polyethylene.

8. As an article of manufacture, long straight ultra-fine fibers of a normally solid synthetic thermoplastic material, said fibers having uniform substantially circular cross-sectional areas throughout their entire length and having average diameters in the range of from 0.5 to 1.0 micron.

9. As an article of manufacture, ultra-fine fibers of a normally solid synthetic thermoplastic resin material, said fibers being molecularly oriented in a longitudinal direction in an amount of between 200 per cent and 2000 per cent and having average diameters in the range of from 0.5 to 1.0 micron.

10. An article of manufacture as claimed in claim 8 in which the normally solid synthetic thermoplastic resin material is one of the group consisting of polyethylene, nylon and polytrifluorochloroethylene.

11. An article of manufacture as claimed in claim 9 in which the normally solid synthetic thermoplastic resin material is one of the group consisting of polyethylene, nylon and polytrifluorochloroethylene.

12. As an article of manufacture a continuous tow of synthetic, normally solid, thermoplastic resin fibers suitable for use in making textiles, said fibers having a substantially circular cross-sectional configuration and having diameters in the range of from 0.1 to 5.0 microns.

13. A process for making woven fabric, having as the warp and the woof, strands of synthetic thermoplastic fibers having diameters in the range of from 0.1 to 5.0 microns, which comprises extruding a mixture having unequal parts by volume of two mutually incompatible synthetic, normally solid, thermoplastic resin materials to form a composite monofilament comprising ultra-fine fibers having diameters of between 0.1 and 5.0 microns, weaving said composite monofilament into fabrics, and selectively dissolving out the major resin component of the composite monofilament.